An Interesting Application of Electron Diffraction *

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SILICOSIS develops rather quickly in rabbits exposed to air containing moderate concentrations of quartz particles finer than about 5×10^{-4} cm, but is completely prevented if aluminum powder is also present in the air to the extent of about one per cent by weight of the quartz powder. This protective action of aluminum powder was discovered at the McIntyre-Porcupine Mines, and has been studied experimentally by Denny, Robson and Irwin.[1]

It has been established that aluminum forms, in the lungs, a protective film upon the surface of silica particles which prevents them from dissolving, and thus prevents toxic effects. From the relative amounts of aluminum and silica, and diameters of silica particles, one can deduce that this protective film need never be so thick, on the average, as 2×10^{-6} cm, and is, in general, many times thinner than this.

The action of the aluminum is sufficiently striking and important to justify a fuller understanding of the nature of the film which it forms upon quartz particles and Dr. Frary, Director of the Aluminum Research Laboratories, suggested to us that the answer might be forthcoming through a study of electron diffraction patterns.

In our experiments, electron diffraction patterns were obtained from thin films of silica, about 2×10^{-6} cm thick, which had been previously treated with water containing metallic aluminum powder. A beam of high speed electrons was sent through such a treated film and the resulting diffraction pattern recorded upon a photographic plate. From studies of such patterns, and comparisons with X-ray and electron patterns of known substances, materials composing layers upon silica surfaces were identified.

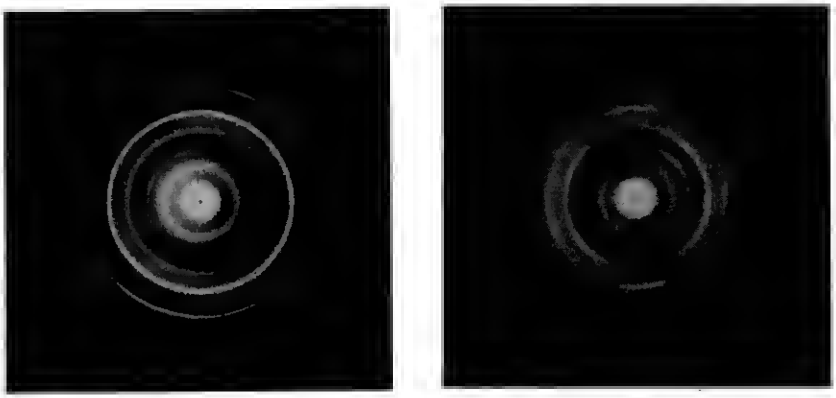
Silica films for these studies were prepared in the following manner. A glass microscope slide was first covered by gold vaporized in high vacuum from a V-shaped tungsten ribbon; then immediately in the same apparatus silica was vaporized upon the gold from a second tung-

* Digest of a paper entitled "Identification of Aluminum Hydrate Films of Importance in Silicosis Prevention," published in *Industrial and Engineering Chemistry*, Anal. Edition, 11, 583 (1939).

[1] J. J. Denny, W. D. Robson and D. A. Irwin, *Canadian Medical Association Journal*, *37*, 1–11 (1937); *40*, 213–228 (1939).

sten ribbon, the distances and the quantities of gold and silica having been adjusted so that the resulting composite film consisted of a layer of silica of thickness 2×10^{-6} cm lying upon a layer of gold of thickness 30×10^{-6} cm. This composite film was large enough to supply a great many samples of silica which could be used in a large number of experiments. Each sample was prepared, as and when required, by stripping from the glass slide a small piece of the composite film, dissolving the gold in a nitric-hydrochloric acid mixture, and then washing the remaining tiny silica film in several changes of distilled water.

Films prepared in this manner were floated upon distilled water containing aluminum powder, for various lengths of time and at two differ-



A B

Fig. 1—Electron diffraction patterns from a relatively thick layer of oriented aluminum alpha-monohydrate crystals formed upon a silica film as a result of exposure of the film to metallic aluminum and water at 38° C. *A*—Electron beam normal to film surface. *B*—Beam inclined 45° to film surface.

ent temperatures. In some experiments the pH of the water was adjusted by the addition of HCl or various salts.

Films treated at 38° C. (approximately body temperature), and at medium and high pH values [2] (6 to 9), gave sharp electron diffraction patterns which were identified with oriented crystals of that hydrated oxide of alumina known as aluminum alpha-monohydrate (Boehmite). Typical patterns are reproduced in Fig. 1. At a low pH value (pH 4) monohydrate crystals were not discovered even after long reaction times. Although the crystal structure of aluminum alpha-monohydrate is not known it was possible to make the identification by

[2] The term pH is defined as the logarithm of the reciprocal of hydrogen ion concentration, hydrogen ion concentration being expressed for purposes of this definition in terms of grams of hydrogen ions in a liter (or more strictly 1000 grams) of solution. In a neutral solution pH = 7; in acid pH < 7 and in alkali pH > 7.

comparison of the electron patterns with X-ray and electron patterns obtained from the bulk material (Fig. 2).

Electron diffraction patterns from alpha-monohydrate formed on silica surfaces were found to vary markedly with pH of the aluminum-water solution and with the reaction time. From these patterns the following conclusions were drawn. Monohydrate crystals formed after short reaction times (4 hours to 20 hours) were sharply oriented with a particular crystal plane parallel to the silica surface; the individual crystals were on the average fairly large (from 5 to 10×10^{-7} cm) in directions parallel to the surface, and thin (2×10^{-7} cm or less) normal to the surface. As the reaction time was increased, the crystals became, on the average, thicker normal to the surface (but seldom

Fig. 2—Electron diffraction pattern obtained by the reflection method from finely pulverized aluminum alpha-monohydrate ($Al_2O_3 \cdot H_2O$).

as thick as 5×10^{-7} cm), and at the same time other crystals of monohydrate were formed which were less nearly perfectly oriented although still showing the same strong preference. For long reaction times layers of completely unoriented alpha-monohydrate crystals were sometimes produced.

In the presence of traces of organic acids oriented soap crystals were formed as a result of the reaction of aluminum and water. These crystals were produced at all pH values. They appeared as scum upon the water surface, and were not readily adsorbed upon silica. This fact proves that the action of aluminum in preventing development of silicosis cannot be attributed to an aluminum soap. Figure 3 exhibits a typical diffraction pattern from oriented crystals of an aluminum soap.

Fig. 3—Electron diffraction pattern produced by a layer of oriented crystals of an aluminum soap, which had been formed as scum upon a water surface as a result of the reaction of powdered aluminum, water and traces of organic acid present as an impurity.

Our experiments prove that aluminum hydrate is precipitated fairly rapidly upon silica at pH values lying within a range in which lie also the pH values of body fluids of men and of animals. Since in these experiments aluminum hydrate is not formed upon silica at pH 4, it seems highly probable that aluminum would not afford protection from silicosis to a hypothetical animal with body fluids of pH 4.